ABSORPTION OF MICRORADIO WAVES BY DIMERS OF ATMOSPHERIC WATER VAPOR

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Abstract

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ABSORPTION OF MICRORADIO WAVES BY DIMERS OF ATMOSPHERIC WATER VAPOR

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In (^{1}) the absorption coefficient of electromagnetic waves by dimers of water vapor was calculated for half-widths of the dimer spectral lines $(\Delta\nu/c)^0_{ij} = 0.2$ and 0.02 cm^{-1}. Here, for the same dimer model, analogous results will be given for half-width values $(\Delta\nu/c)^0_{ij} = 0.4;\ 0.8;\ 1.6$ cm^{-1} (see Fig. 1).

Fig. 1. 1 –absorption coefficient of monomers of atmospheric water vapor; 2, 3, 4 –absorption coefficient of dimers of atmospheric water vapor for half-widths of their spectral lines $(\Delta\nu/c)_{ij} = 0.4$ cm^{-1} (2), 0.8 cm^{-1} (3); 1.6 cm^{-1} (4). $T = 293°$, $p = 760$ mm Hg, $\rho = 7.5$ g/m^3, $\varepsilon = 4.8$ kcal/mol

In Fig. 1 curve 1 shows the absorption coefficient γ (dB/km) by monomers of atmospheric water vapor at a temperature of 293°K, pressure of 760 mm Hg, and absolute humidity $\rho = 7.5$ g/m^3. The calculation was performed by formula (15) of work (^{2}). The half-widths of the spectral lines of the monomer 5_{-1}—6_{-5} ($\lambda_{ij} = 1.35$ cm), 2_2—3_{-2} ($\lambda_{ij} = 1.63$ mm), 4_0—5_{-4} ($\lambda_{ij} = 0.92$ mm), 3_1—4_{-3} ($\lambda_{ij} = 0.789$ mm), 1_{-1}—1_1 ($\lambda_{ij} = 0.538$ mm), according to experiment (see the review (^{3})), were taken to be respectively $(\Delta\nu/c)^0_{\mathrm{H_2O-vap}} = 0.084;\ 0.107;\ 0.106;\ 0.106;\ 0.118$ cm^{-1}, while the half-widths of the other lines of the mono-

the H O monomer are larger by a factor of 1.2 in comparison with the calculation of Benedict and Kaplan ( ).

Curves 2, 3, and 4 in Fig. 1 represent the absorption coefficient γ_{dim} (dB/km) by water-vapor dimers at $T = 293°$ K and a dimer concentration $\rho_{\mathrm{dim}} = 0.0122$ g/m^3, corresponding, according to formula (2) of paper (^{1}), to a temperature of 293°, a dimer binding energy $\varepsilon = 4.8$ kcal/mol*, and an absolute humidity $\rho = 7.5$ g/m^3, for identical half-widths of all dimer spectral lines equal to $(\Delta\nu/c)^0_{ij} = 0.4;\ 0.8;\ 1.6$ cm^{-1}. The calculation was carried out using formula (1) of paper (^{1}), exactly as for the half-widths $(\Delta\nu/c)^0 = 0.02;\ 0.2$ cm^{-1} (^{1}); it describes the rotational spectrum of the dimer (^{1}).

The real values of the half-widths $(\Delta\nu/c)^0_{ij}$ of the dimer spectral lines in air are at present unknown. However, because of the large size of the dimer compared with the monomer, the half-widths of the dimer spectral lines must exceed the half-widths of the monomer spectral lines. The latter values under atmospheric conditions at sea level are about 0.1 cm^{-1}. Since the linear dimensions of the dimer molecule are approximately twice those of the monomer, one should expect the gas-kinetic effective collision cross section of the dimer to be ~ 4 times larger than that of the monomer. Taking into account, moreover, the greater closeness of its rotational energy levels (compared with the monomer), due to its large moments of inertia and internal rotation, one may suppose that the optical effective collision cross section of the dimer exceeds that of the monomer not by 4, but by a larger number of times. We are inclined to think that under atmospheric conditions at sea level the half-widths of the dimer spectral lines will be of the order of $(\Delta\nu/c)^0_{ij} \approx 0.8\ \mathrm{cm}^{-1}$.

Fortunately, the absence of exact data on the half-widths of the dimer spectral lines under atmospheric conditions at sea level has little effect on the calculated value of the absorption coefficient γ_{dim} caused by it. Since the intensities of the spectral lines of the P- and R-branches of the dimer (at least at wavelengths $\lambda < 2$ mm) vary very smoothly with frequency, while the distance between them (for the same value of the vibrational quantum number v) is 0.46 cm^{-1} ( ), i.e., of the order of (and smaller than) the dimer line half-widths $(\Delta\nu/c)^0_{ij}$ just indicated, under atmospheric conditions at sea level the spectral lines become smeared, so that (at least at wavelengths $\lambda < 2$ mm and outside the maxima of the Q-branch centered at $\lambda^{-1} = 7.07$ and 21.21 cm^{-1}) the dimer absorption coefficient proves to be practically independent of the half-width $(\Delta\nu/c)^0_{ij}$. The calculation confirms these considerations (see Fig. 1).

That the half-width value 0.8 cm^{-1} is preferable to the value 0.4 cm^{-1} under atmospheric conditions at sea level is indicated, in addition to the arguments given above, by the fact that for $(\Delta\nu/c)^0_{ij} \leqslant 0.4\ \mathrm{cm}^{-1}$ a noticeable absorption peak due to the Q-branch should appear at $\lambda^{-1} \approx 7.07\ \mathrm{cm}^{-1}$, whereas for $(\Delta\nu/c)^0_{ij} \geqslant 0.8$ it is smoothed out (see Fig. 1); the measurements of paper ( ), as well as the measurements of V. Ya. Ryadov and N. I. Furashov ( ), do not reveal such a peak.

It is seen from Fig. 1 that, at wavelengths longer than 1 mm, dimers in the transparency windows of monomers make approximately the same contribution to absorption as the latter (this statement applies especially to summer conditions, when $\rho \approx 15\ \mathrm{g/m}^3$, so that γ_{dim} increases by a factor of 4, whereas γ_{mon} increases only by a factor of 2 compared with the values shown in Fig. 1). The contribution of dimers continues to remain comparable with the contribution of monomers also at shorter wavelengths, down to $\lambda \approx 0.7$ mm. At wavelengths shorter than 0.7 mm, the rotational

* The binding energy is taken equal to $\varepsilon = 4.8$ kcal/mol for better agreement with the experimental data (see below); in papers (,) the dimer binding energy was assumed equal to $\varepsilon = 5.2$ kcal/mol, which gave a larger dimer concentration,

$\rho_{\text{dim}} = 0.022$ g/m^3.

the absorption spectrum of the dimers, as is seen from Fig. 1, already plays only a minor role.

Calculations of the absorption coefficient of the dimers, performed for $(\Delta\nu/c)^0_{ij} = 0.8$ cm^{-1} in the temperature interval 293—233°K, showed that, at a fixed concentration of dimers, the temperature dependence of the absorption coefficient can be approximated in the indicated interval by the expression

$$\gamma_{\text{dim}} = Ce^{164/T - \alpha(\lambda)} \tag{1}$$

(the appearance of the factor $\exp(164/T)$ is due to the internal rotation of the dimer). The wavelength-dependent exponent $\alpha(\lambda)$ is given in Table 1 (the scatter of the exponent $\alpha(\lambda)$ indicated therein determines the limits of its values in the temperature interval 293—233°K).

Table 1

λ^{-1}, cm^{-1}	0.5	1	2.5	5	6.75
$\alpha(\lambda)$	2.815 ± 0.004	2.778 ± 0.006	2.64 ± 0.01	2.47 ± 0.01	2.28 ± 0.01
λ^{-1}, cm^{-1}	10	15	20	25	30
$\alpha(\lambda)$	2.26 ± 0.03	1.66 ± 0.06	1.13 ± 0.05	0.42 ± 0.02	0.23 ± 0.1

Taking into account the temperature dependence of the concentration of dimers (see formula (2) of paper (^{1})) and the temperature dependence of the absorption coefficient of the dimers at a fixed concentration of the latter (see formula (1) and Table 1), the total absorption coefficient of atmospheric water vapor $\gamma_{\text{water vapor}}$ can be represented by the approximate formula

$$\gamma_{\text{water vapor}}\left[\frac{\text{db}}{\text{km}}\right] = \gamma_{\text{mon}}(\lambda)\frac{\rho}{7.5}\left(\frac{T}{293}\right)^{-5/2}\frac{p}{760} + \gamma_{\text{dim}}(\lambda)\left(\frac{\rho}{7.5}\right)^2\left(\frac{T}{293}\right)^{-\alpha(\lambda)} e^{532.9(\varepsilon/T - 4.8/293)} \tag{2}$$

where the first term describes absorption by monomers, and the second, absorption by water-vapor dimers. The coefficients $\gamma_{\text{mon}}(\lambda)$ and $\gamma_{\text{dim}}(\lambda)$ do not depend on the air humidity ρ, temperature T, and pressure p, and are determined, respectively, by curves 2 and 3 (at $(\Delta\nu/c)^0_{ij} = 0.8$ cm^{-1}) in Fig. 1. For a dimer binding energy $\varepsilon = 4.8$ kcal/mole, in the temperature interval $313 \div 233$°K with an error of less than 8%, and in the temperature interval 300—243°K with an error of less than 3%, the second (dimer) term of formula (2) can be approximated by a power function. Then (2) takes the form

$$\gamma_{\text{water vapor}}\left[\frac{\text{db}}{\text{km}}\right] = \gamma_{\text{mon}}(\lambda)\frac{\rho}{7.5}\left(\frac{T}{293}\right)^{-5/2}\frac{p}{760}+\gamma_{\text{dim}}(\lambda)\left(\frac{\rho}{7.5}\right)^{2}\left(\frac{T}{293}\right)^{-\alpha(\lambda)-8.9}. \tag{3}$$

Conditions of applicability of formulas (2), (3):

1. The wavelength λ lies within the limits 0.3 mm $< \lambda < 2$ mm and does not fall on monomer resonances or on the peaks of the Q-branch, $\lambda^{-1} \approx 7.07;\ 21.21$ cm^{-1} (for $\lambda > 2$ mm and $\lambda^{-1} \approx 7.07;\ 21.21$ cm^{-1}, according to Fig. 1, the atmospheric absorption of dimers begins to depend noticeably on the half-widths of the spectral lines, and hence also on the pressure p).
2. The humidity ρ is not too large ($\rho < 15$ g/m^3, so that the increase in the half-widths of the spectral lines of the monomers due to the role of H_2O—H_2O collisions may be neglected).
3. The temperature lies within the limits $233^\circ < T < 300^\circ$.
4. The pressure p is not too small (at $p \lesssim \frac{1}{4} \cdot 760$ mm Hg resolution of the spectrum of water-vapor dimers sets in; see Fig. 1 of paper (^{1}), the absorption curve at $(\Delta\nu/c)^0_{ij} = 0.2$ cm^{-1}).

The processing, carried out by V. Ya. Ryadov and N. I. Furashov (^{8}), using formula (3), of the results of measurements of the absorption coefficient of air by the variable-humidity method at wavelengths 0.73; 0.87; 1.4 mm showed that, at these wavelengths, if the monomer absorption is taken to be equal to the theoretical-

with spectral-line half-widths 20% greater than the values of Benedict and Kaplan ( ) (see the first term of formula (3) and curve 1 (Fig. 1)), the magnitude of the dimer absorption is obtained as 1.3–2 times smaller than the theoretical value (for a dimer concentration corresponding to a binding energy $\varepsilon = 4.8$ kcal/mole). However, as V. Ya. Ryadov and N. I. Furashov informed us, recently they have arrived at a value of the half-width of the strongest of the spectral lines measured by them, 1_{-1}—1_1 (0.538 mm), close to the theoretical value ( ), so that, apparently, the increase of the half-widths of the shorter-wavelength lines (as was done by us in the extrapolation procedure) is at present unjustified. In this case the monomer absorption in the "windows" will decrease by $\sim 15\%$ in comparison with that shown in the upper plot of Fig. 1, as a result of which the "experimental" dimer absorption will increase by a factor of 1.5–2 and at wavelengths 0.73; 0.87; 1.4 mm will be close to the theoretical value (for a dimer concentration corresponding to a binding energy $\varepsilon = 4.8$ kcal/mole). At wavelengths of ~ 1 cm, processing ( ) of the measurement results (^{1}) gives a value of the dimer absorption ~ 2 times greater than the theoretical value (for $(\Delta\nu/c)^0_{ij} = 0.8$ cm^{-1}). We note that if the spectral-line half-widths of the dimer are taken equal to $(\Delta\nu/c)^0_{ij} = 1.6$ cm^{-1}, then at $\varepsilon = 4.8$ kcal/mole one can obtain agreement between the theoretical and experimental values of the dimer absorption coefficient over the entire range considered.

In conclusion, we note that, in comparison with ( ), the magnitude of the dimer absorption of the atmosphere has now decreased by a factor of 4 (by a factor of 2.1 owing to allowance for the anharmonicity of internal rotation and by a factor of 2 owing to the decrease in the dimer concentration as a result of the decrease of the dimer binding energy from 5.2 to 4.8 kcal/mole).

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Note: Figure translations are in progress. See original paper for figures.